A Ph. D. thesis by

Thomas Erwin Phipps

THE CONDUCTANCE OF CERTAIN ALKALI METALS IN LIQUID AMMONIA AND IN METHYLAMINE

The photometric investigation by Gibson and Argo[1] of the blue solutions of several alkali and alkaline earth metals in liquid ammonia and in methylamine led to identical absorption curves in liquid ammonia, but to more complex ones in methylamine. The hypothesis was advanced that in liquid ammonia the dissociation of the metal into electrons is nearly complete, and that the solvation of these electrons is nearly complete; whereas in methylamine the concentration of the unionized metal is considerable, and the solvation of the electrons is incomplete. The most promising method of studying the interesting questions of ionization and solvation appeared to be in determining the temperature coefficients of conductivity of the blue solutions in liquid ammonia and in methylamine .

Since liquid ammonia was more available than methylamine, it was used as solvent in all earlier experiments, and later when the manipulation was well established, solutions in methylamine were studied. While the investigation was in progress, the recent comprehensive study by Kraus[2] of conductances in liquid ammonia was published, and his results are confirmed at several points by our own.

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1 Gibson and Argo, Phys. Rev., 1, 33 (1916); This Journal, 40, 1327 (1916).

2 Kraus, This Journal, 43, 749 (1921).

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Deposited in the Library Sept. 19, 1922

The photometric investigation by Gibson and Argo[1] of the blue solutions of several alkali and alkaline earth metals in liquid ammonia and in methylamine led to identical absorption curves in liquid ammonia, but to more complex ones in methylamine. The hypothesis was advanced that in liquid ammonia the dissociation of the metal into electrons is nearly complete, and that the solvation of these electrons is nearly complete; whereas in methylamine the concentration of the unionized metal is considerable, and the solvation of the electrons is incomplete. The most promising method of studying the interesting questions of ionization and solvation appeared to be in determining the temperature coefficients of conductivity of the blue solutions in liquid ammonia and in methylamine.

Since liquid ammonia was more available than methylamine it was used as solvent in all earlier experiments, and later when the manipulation was well established, solutions in methylamine were studied. While the investigation was in progress, the recent comprehensive study by Kraus[2] of conductances in liquid ammonia was published, and his results are confirmed at several points by our own.

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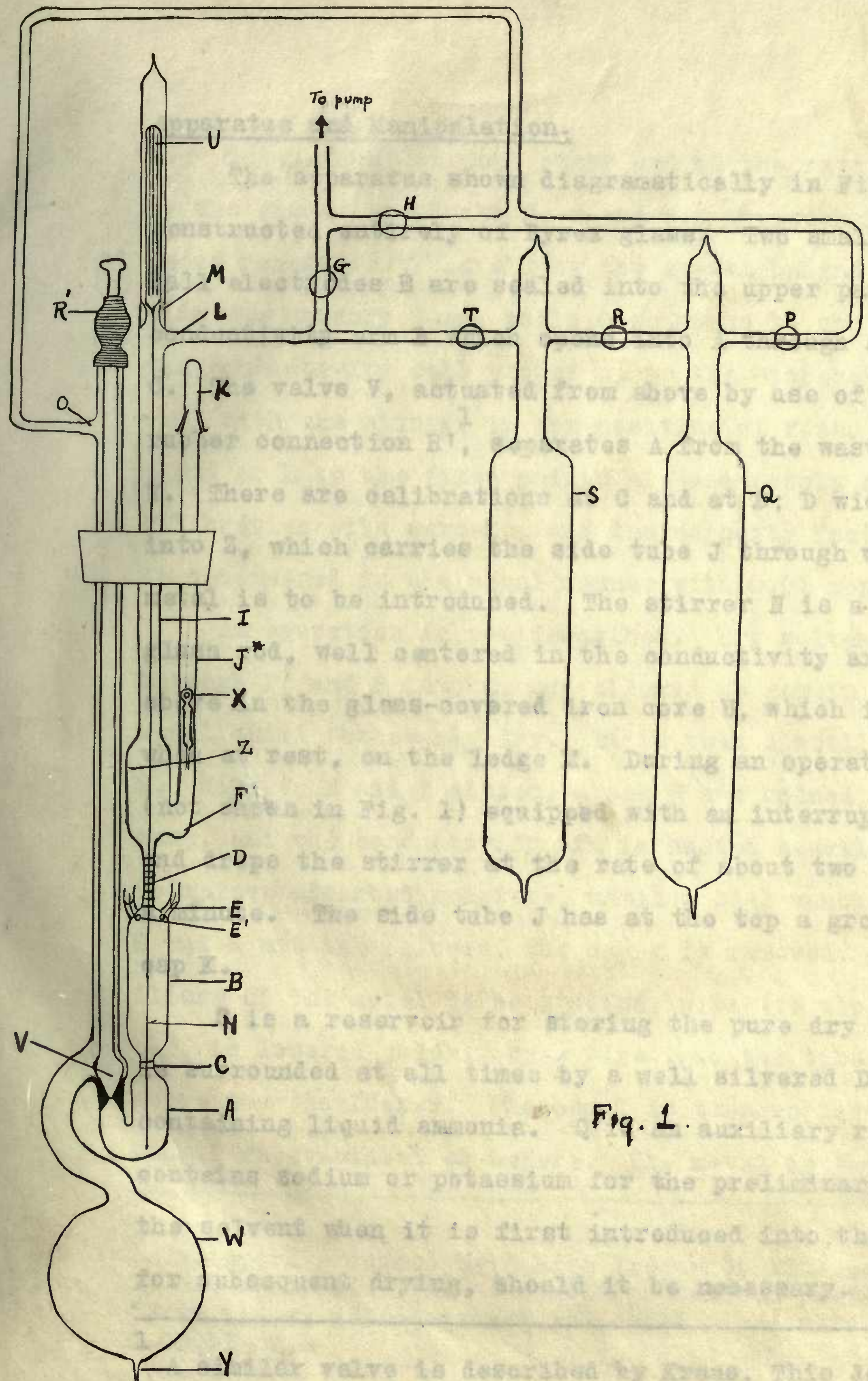

Fig. 1

* The side-tube J enters Z at a point higher than that shown in the figure.

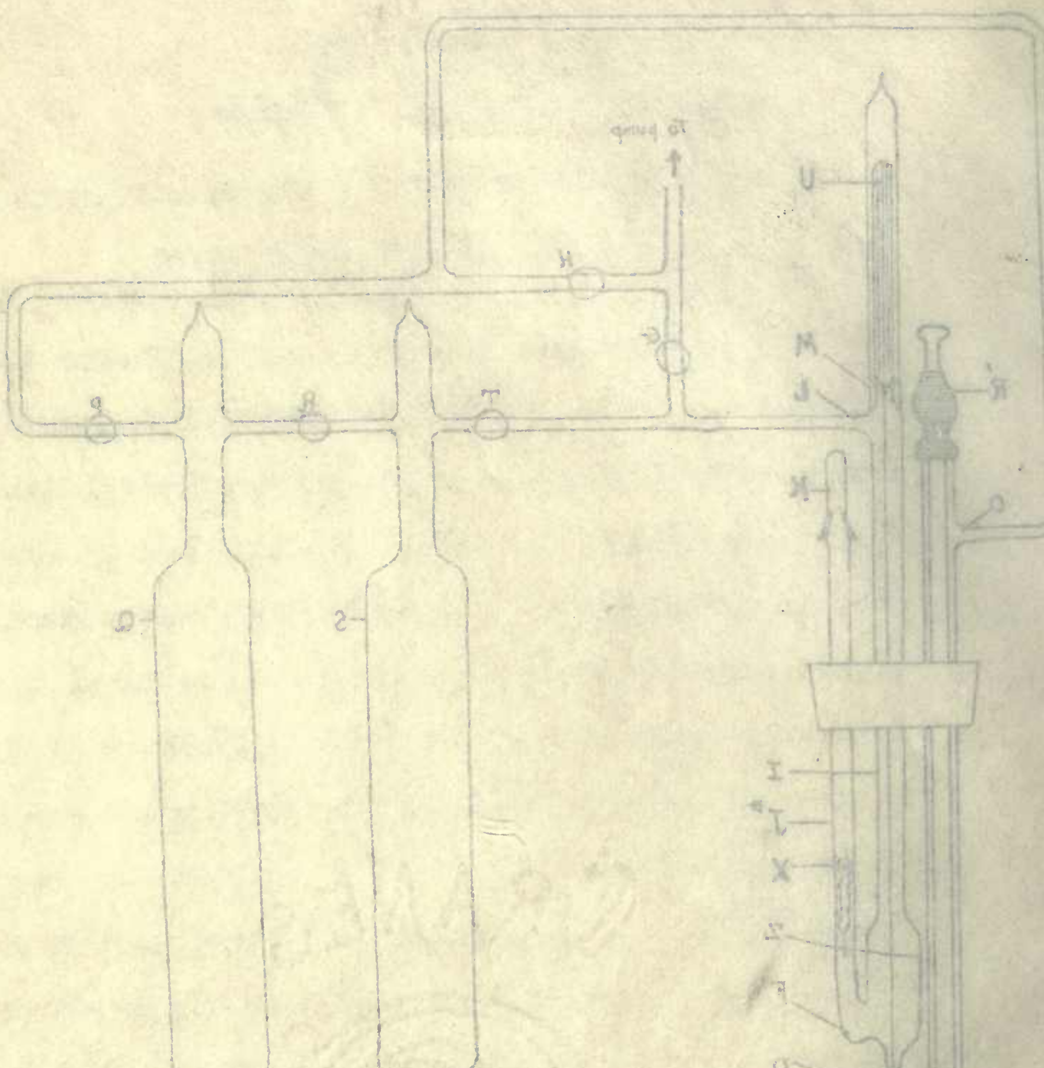

Fig. 1

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* The side-tube J enters S at a point higher than that shown in

Apparatus and Manipulation.

The apparatus shown diagramatically in Fig. 1 is constructed entirely of Pyrex glass. Two small platinum ball electrodes E are sealed into the upper part of the conductivity arm B which opens into A through a constriction C. The valve V, actuated from above by use of the taut rubber connection R'[1], separates A from the waste reservoir W. There are calibrations at C and at D; D widens above into Z, which carries the side tube J through which the metal is to be introduced. The stirrer N is a very slender glass rod, well centered in the conductivity arm, terminating above in the glass-covered iron core U, which is supported, when at rest, on the ledge M. During an operation, a solenoid (not shown in Fig. 1) equipped with an interruptor lifts and drops the stirrer at the rate of about two hundred times a minute. The side tube J has at the top a ground glass cap K.

S is a reservoir for storing the pure dry solvent, and is surrounded at all times by a well silvered Dewar vessel containing liquid ammonia. Q is an auxiliary reservoir which contains sodium or potassium for the preliminary drying of the solvent when it is first introduced into the system, and for subsequent drying, should it be necessary. S and Q are

[1] A similar valve is described by Kraus, This Journal, 36,866(

made independent of each other and of the rest of the system by the vacuum stopcocks T, r and P. Stopcock H connects the waste reservoir W and all of the system behind the valve V with the mercury pump, while G connects to the pump all of the conductivity cell proper up to the stopcock T.

With the stirrer in its position of rest, the volumes of A and of B to the fixed points are accurately determined by calibration with mercury, and the capacity factor of the cell is determined in the usual manner with 0.01 normal KCl.

An operation is now described. Dry solvent is distilled through P' and P into Q, and allowed to remain there on the metal until thoroughly dry. It is then distilled into S throug R. With P, R and T closed, G and H are opened to the mercury pump, and the conductivity arm is heated heavily with a flame to remove adsorbed moisture, until a high vacuum is obtained.[1] G and H are then closed, the cap K is removed, and a capillary of the metal to be studied, with its tip freshly broken off, is lowered quickly by a wire into the tube J to a point above the shoulder F. The cap K is then replaced and the vessel re-evacuated as before. The metal is then melted out

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1 The spark produced by a high frequency 110v coil was entirely extinguished. When a similar condition prevailed in other Pyrex lines, McLeod guages indicated a pressure of less than 0.00001 mm.

of the capillary by gentle heating of J, and rests as a bright globule in F, whence by further heating it is distilled, in whole or in part as desired, into the wider tube Z where it appears as a bright mirror on the walls of the glass. Potassium and caesium distill very rapidly, and even sodium distills quite readily in a very high vacuum. The slight amount of oxide which accompanied the introduction of the capillary remains in F throughout the run, and solvent is never condensed on it.

G and H are then closed, and the conductivity cell is surrounded by a bath of boiling liquid ammonia with its level at Z. Dry solvent is then distilled through T from the reservoir S, and the metal is completely washed down into A and B until the blue solution fills the vessel from the valve up to a point in D. Stirring is continued till the conductivity reaches a constant value, when the volume is read with the stirrer at rest.

To make a dilution, the bath is lowered away for a moment till its level is at C, and the valve is slightly unseated by upward tension at R' until the level of the blue solution has fallen to C. With a well ground valve this regulation is very accurate. The bath is then replaced and fresh solvent distilled in as before, with the stirrer

operating all the while. At the end of a run, which rarely required more than two hours, stopcocks H, P and R are opened and the solvent is returned by distillation from the blue solution in W to S, leaving in W all the metal which was originally present in the first solution. With the solvent isolated in S, the last trace of solvent is removed from the metal by evacuation and by slight warming of W. The tip Y is then broken, and the metal is oxidized by a stream of moist air admitted at P'. W is then washed out thoroughly, the solution is evaporated to a small volume to remove ammonia, and the solution is titrated with 0.1 normal HCl, with methyl orange as an indicator.[1] All necessary data are now at hand for the calculation of volume-normal concentrations and specific and molecular conductivities.

To prepare the vessel for another run, the empty capillary X is withdrawn and the vessel filled through J down as far as the valve with cleaning mixture, which is then heated and allowed to stand in the vessel for several minutes. It is forced out by way of V through Y, and followed by many changes of distilled water, which is removed in the same way. Finally, with the valve clamped open, the vessel is dried thoroughly by a stream of warm air coming from P' and from K. The tips Y and P' are sealed off and the evac-

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[1] Alcohol was not used on account of the uncertainty of the end-point when it was present.

uation proceeds as before.

The filling of capillaries is as follows: tubing of small bore is constricted further, and bent at about a 60° angle at the constriction. One end of the tube is sealed off at a suitable distance from the bend, and the other end is sealed to a vacuum line. After being evacuated, the tube is sealed off at a point which leaves a symmetrical V-shape. The tip of the "V" is put below the surface of a globule of the molten metal and broken; this leaves the two tubes terminating in small capillaries entirely filled with bright clean metal. To prevent further oxidation of the metal at the tips, the capillaries are kept under oil.

The two temperatures employed in most of the experiments were the boiling point of liquid ammonia, and a temperature about 15° lower ($-48.5^\circ C$), obtained by bubbling dried air at a controlled rate through the bath. By hand regulation the temperature was kept constant within $0.1^\circ C$ or $0.2^\circ C$. Chloroform, frozen by means of solid carbon dioxide was used as a bath in two or three of the experiments, but its temperature was found to be quite inconstant, and because of the difficulty of making a satisfactory constant temperature bath in the neighborhood of $-70.0^\circ C.$, work at the lower temperature was abandoned, although on account of slower fading it seemed desirable to work at that temperature.

Results.

The work in liquid ammonia comprised measurements at three temperatures, $-33.5^\circ C$, $-48.5^\circ C$, and $-70.0^\circ C$. of the conductivities of the blue solutions of sodium between concentrations of 0.4 normal and 0.0001 normal, and measurements at the first two temperatures of potassium solutions. Curves I, II and III of Fig. 2 show the specific conductance as a function of the "dilution" V, and Curves I', II' and III' show the molecular conductivity Λ as a function of V. The agreement between the different runs is good as far as 0.001 normal, but beyond that concentration the "fading"[1] is appreciable and erratic. At $-33.5^\circ C$. the highest value for log k at log $V = 4.0$ (0.0001 normal) corresponded to a molecular conductivity of 970, which is lower than the best value of Kraus,[1]- about 1000 at this dilution.

Since the concentrations dealt with here are volume-normal, whereas Kraus's concentrations were weight normal, a direct comparison of the two would involve a knowledge of the densities; or assuming the accuracy of the two sets of data, the densities could be calculated. Unfortunately our measurements do not extend into the most concentrated blue solutions where the densities are most abnormal. A careful comparison of two representative series obtained by

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Table I

Conductance of Sodium in Liquid Ammonia

-33.5° C.

Series I

No.	log k	log V	Λ
1	0.198	0.111	2038
2	$\bar{1}.490$	0.406	787
3	$\bar{1}.074$	0.696	587
4	$\bar{2}.710$	0.985	495
5	$\bar{2}.387$	1.277	461
6	$\bar{2}.116$	1.561	475
7	$\bar{3}.877$	1.844	526
8	$\bar{3}.657$	2.125	605
9	$\bar{3}.422$	2.419	693
10	$\bar{3}.172$	2.708	759
11	$\bar{4}.907$	2.996	799
12	$\bar{4}.633$	3.283	825
13	$\bar{4}.354$	3.576	852

Series II

No.	log k	log V	Λ
1	$\bar{2}.978$	0.793	591
2	$\bar{2}.431$	1.237	466
3	$\bar{2}.019$	1.680	501
4	$\bar{3}.662$	2.125	613
5	$\bar{3}.301$	2.569	742
6	$\bar{4}.882$	3.013	786

Series III

No.	log k	log V	Λ
1	$\bar{2}.896$	0.849	556
2	$\bar{2}.382$	1.295	476
3	$\bar{3}.975$	1.739	518
4	$\bar{3}.625$	2.182	642
5	$\bar{3}.260$	2.625	769
6	$\bar{4}.834$	3.068	798
7	$\bar{4}.329$	3.511	692

Series IV

No.	log k	log V	Λ
1	$\bar{2}.585$	1.087	470
2	$\bar{2}.138$	1.530	466
3	$\bar{3}.772$	1.973	556
4	$\bar{3}.418$	2.416	683
5	$\bar{3}.025$	2.859	766
6	$\bar{4}.592$	3.302	780
7	$\bar{4}.084$	3.745	675

-48.5° C.

Series V

No.	log k	log V	Λ
1	$\bar{1}.062$	0.641	505
2	$\bar{2}.500$	1.086	386
3	$\bar{2}.023$	1.531	358
4	$\bar{3}.630$	1.984	412
5	$\bar{3}.282$	2.427	512
6	$\bar{4}.910$	2.870	603
7	$\bar{4}.472$	3.320	620

Series VI

No.	log k	log V	Λ
1	$\bar{1}.200$	0.536	545
2	$\bar{2}.616$	0.981	396
3	$\bar{2}.120$	1.423	349
4	$\bar{3}.715$	1.873	388
5	$\bar{3}.359$	2.322	480
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7	$\bar{3}.877$	1.844	526
8	$\bar{3}.657$	2.125	605
9	$\bar{3}.482$	2.419	693
10	$\bar{3}.172$	2.708	759
11	$\bar{4}.907$	2.996	799
12	$\bar{4}.653$	3.285	825
13	$\bar{4}.354$	3.576	852

Series II

No.	log k	log V	Λ
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Series IV

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1	$\bar{2}.585$	1.087	470
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3	$\bar{3}.772$	1.973	556
4	$\bar{3}.418$	2.416	683
5	$\bar{3}.025$	2.859	765
6	$\bar{4}.592$	3.302	780
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Series VI

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3	$\bar{2}.120$	1.423	349
4	$\bar{3}.715$	1.873	388
5	$\bar{3}.359$	2.322	480
6	$\bar{4}.975$	2.765	550

Table I (concluded)

-48.5° C.

Series VII

No.	log k	log V	Λ
1	$\bar{2}.850$	0.804	451
2	$\bar{2}.310$	1.248	361
3	$\bar{3}.872$	1.694	368
4	$\bar{3}.508$	2.139	444
5	$\bar{3}.156$	2.584	550
6	$\bar{4}.728$	3.028	570

-70.0° C.

Series VIII

No.	log k	log V	Λ
1	$\bar{2}.836$	0.654	309
2	$\bar{2}.436$	0.971	256
3	$\bar{2}.056$	1.302	228
4	$\bar{3}.723$	1.636	229
5	$\bar{3}.448$	1.963	257
6	$\bar{3}.168$	2.294	290
7	$\bar{4}.896$	2.615	324
8	$\bar{4}.611$	2.935	351
9	$\bar{4}.321$	3.256	360

Series IX

No.	log k	log V	Λ
1	$\bar{1}.295$	0.310	403
2	$\bar{2}.679$	0.778	287
3	$\bar{2}.121$	1.238	229
4	$\bar{3}.657$	1.700	228
5	$\bar{3}.289$	2.162	283
6	$\bar{4}.933$	2.625	362
7	$\bar{4}.547$	3.092	436

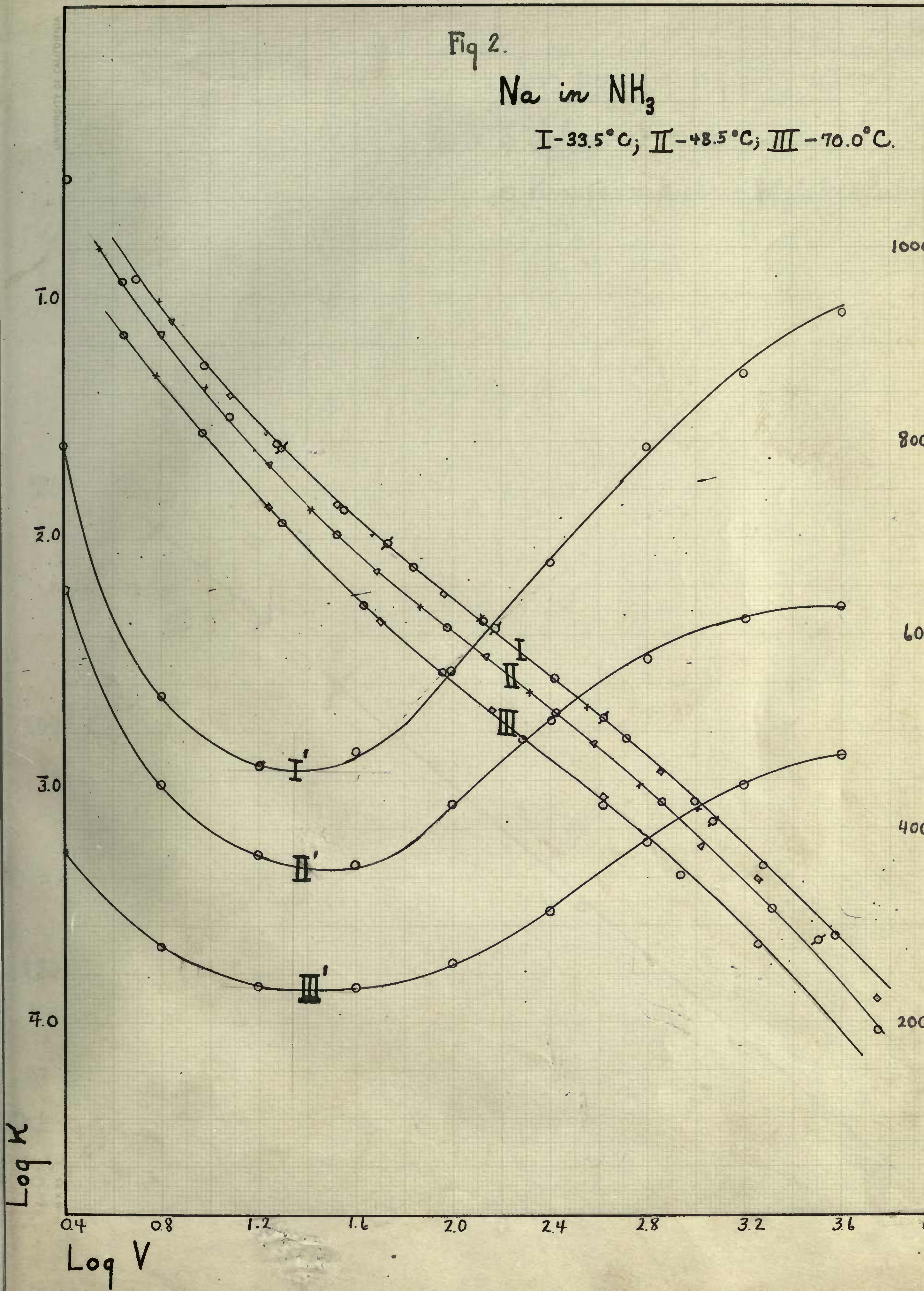
Fig 2.
Na in NH_3
I -33.5°C; II -48.5°C; III -70.0°C.
I
II
III
I'
II'
III'
$\bar{1}.0$
$\bar{2}.0$
$\bar{3}.0$
$\bar{4}.0$
1000
800
600
400
200
0.4
0.8
1.2
1.6
2.0
2.4
2.8
3.2
3.6
Log V
Log K


2
2.0
1.5
Log R

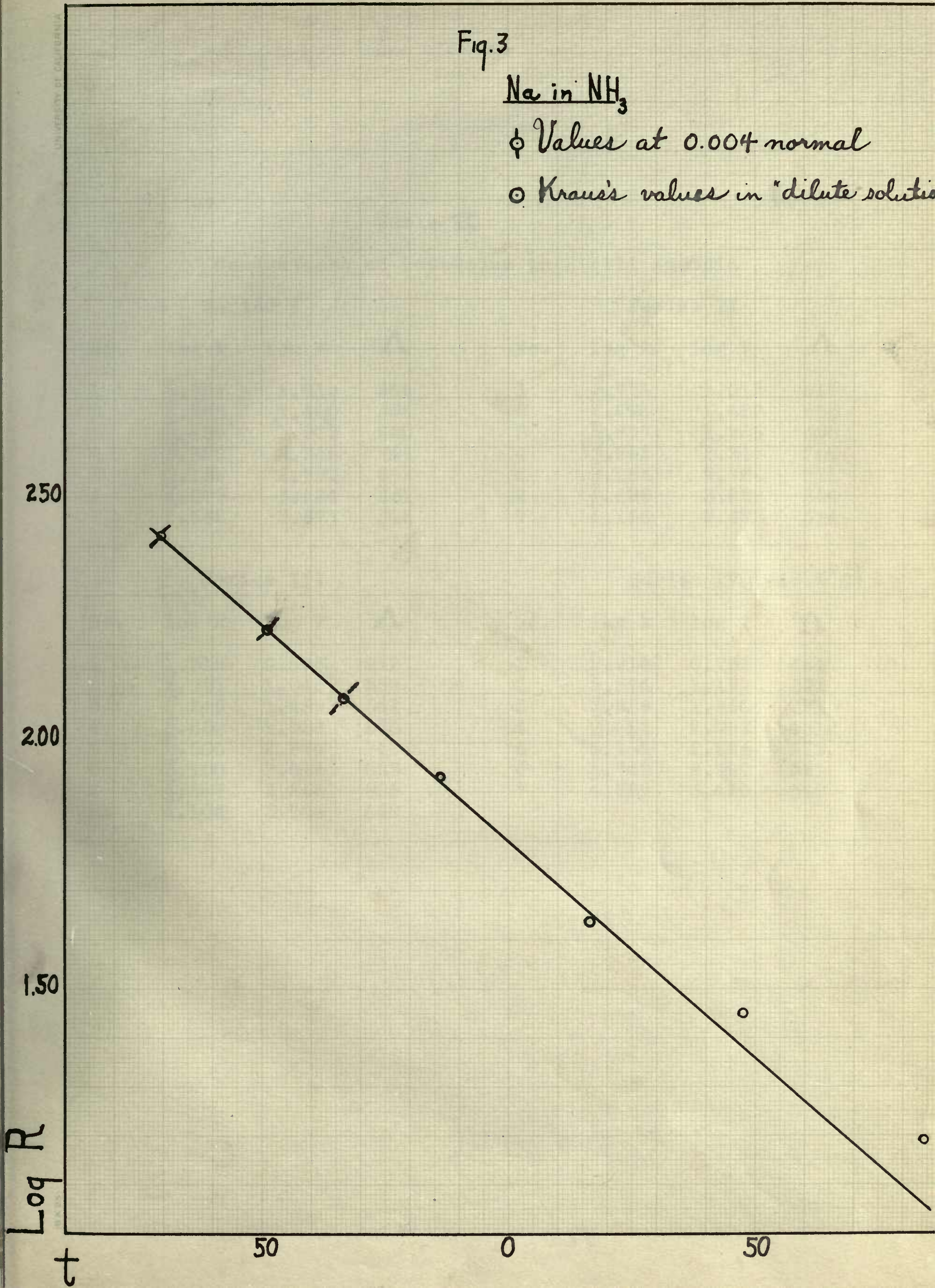
Fig.3
Na in NH_3
Values at 0.004 normal
Kraus's values in "dilute solutio
2.50
2.00
1.50
Log R
t
50
0
50

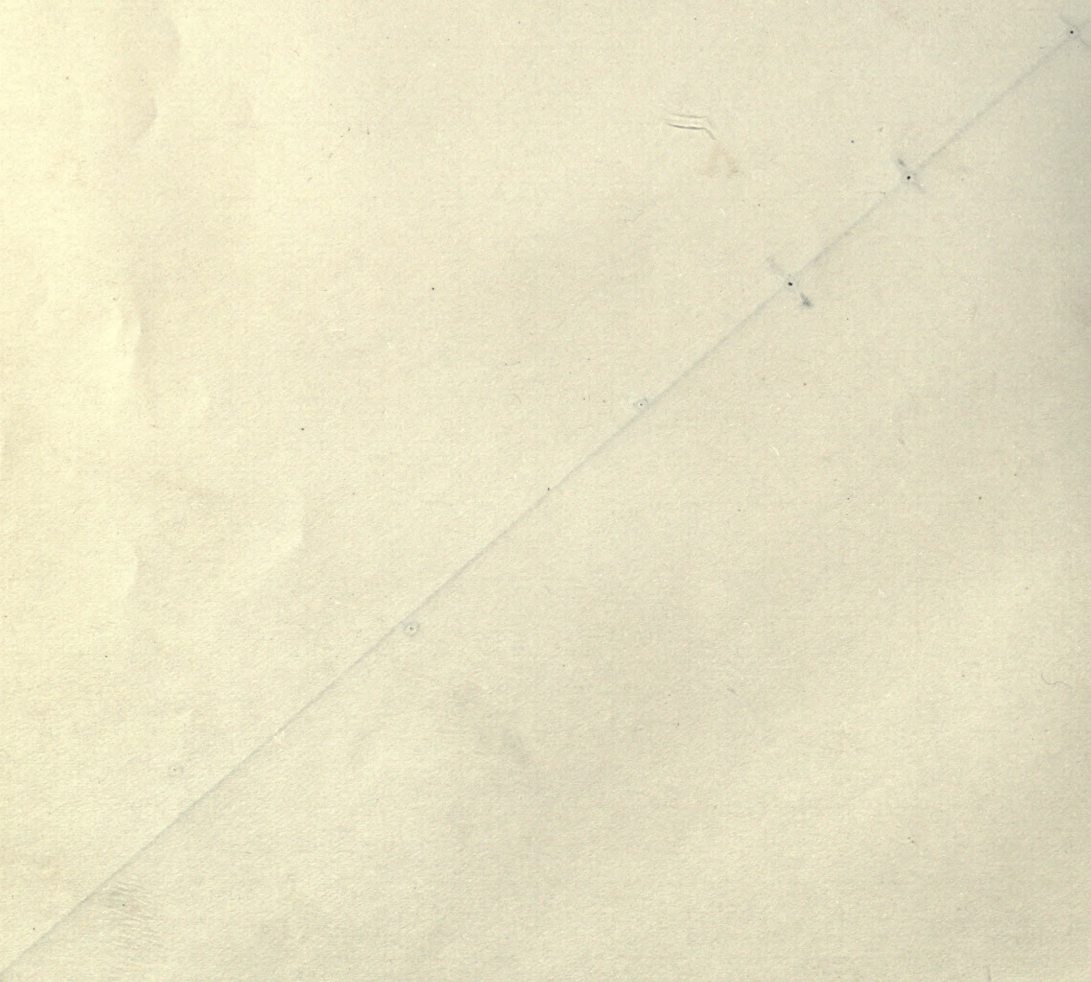

Table II

Conductance of Potassium in Liquid Ammonia

Series I

No.	log k	log V	Λ
1	$\bar{2}.766$	1.015	604
2	$\bar{2}.283$	1.460	554
3	$\bar{3}.889$	1.903	620
4	$\bar{3}.526$	2.346	746
5	$\bar{3}.135$	2.790	842
6	$\bar{4}.579$	3.234	651
7	$\bar{5}.862$	3.677	346

Series II

No.	log k	log V	Λ
1	$\bar{2}.774$	1.015	615
2	$\bar{2}.292$	1.458	563
3	$\bar{3}.897$	1.901	628
4	$\bar{3}.542$	2.344	769
5	$\bar{3}.154$	2.786	871
6	$\bar{4}.698$	3.228	844
7	$\bar{4}.168$	3.673	694

Series III

No.	log k	log V	Λ
1	$\bar{1}.315$	0.595	813
2	$\bar{2}.731$	1.045	598
3	$\bar{2}.245$	1.489	542
4	$\bar{3}.860$	1.932	620
5	$\bar{3}.500$	2.374	749
6	$\bar{3}.100$	2.815	823
7	$\bar{4}.647$	3.258	805
8	$\bar{4}.103$	3.703	640

Series IV (-48.5°C)

No.	log k	log V	Λ
1	$\bar{2}.914$	0.752	464
2	$\bar{2}.374$	1.197	373
3	$\bar{3}.929$	1.640	371
4	$\bar{3}.552$	2.082	431
5	$\bar{3}.185$	2.524	512
6	$\bar{4}.749$	2.967	521
7	$\bar{4}.329$	3.410	549

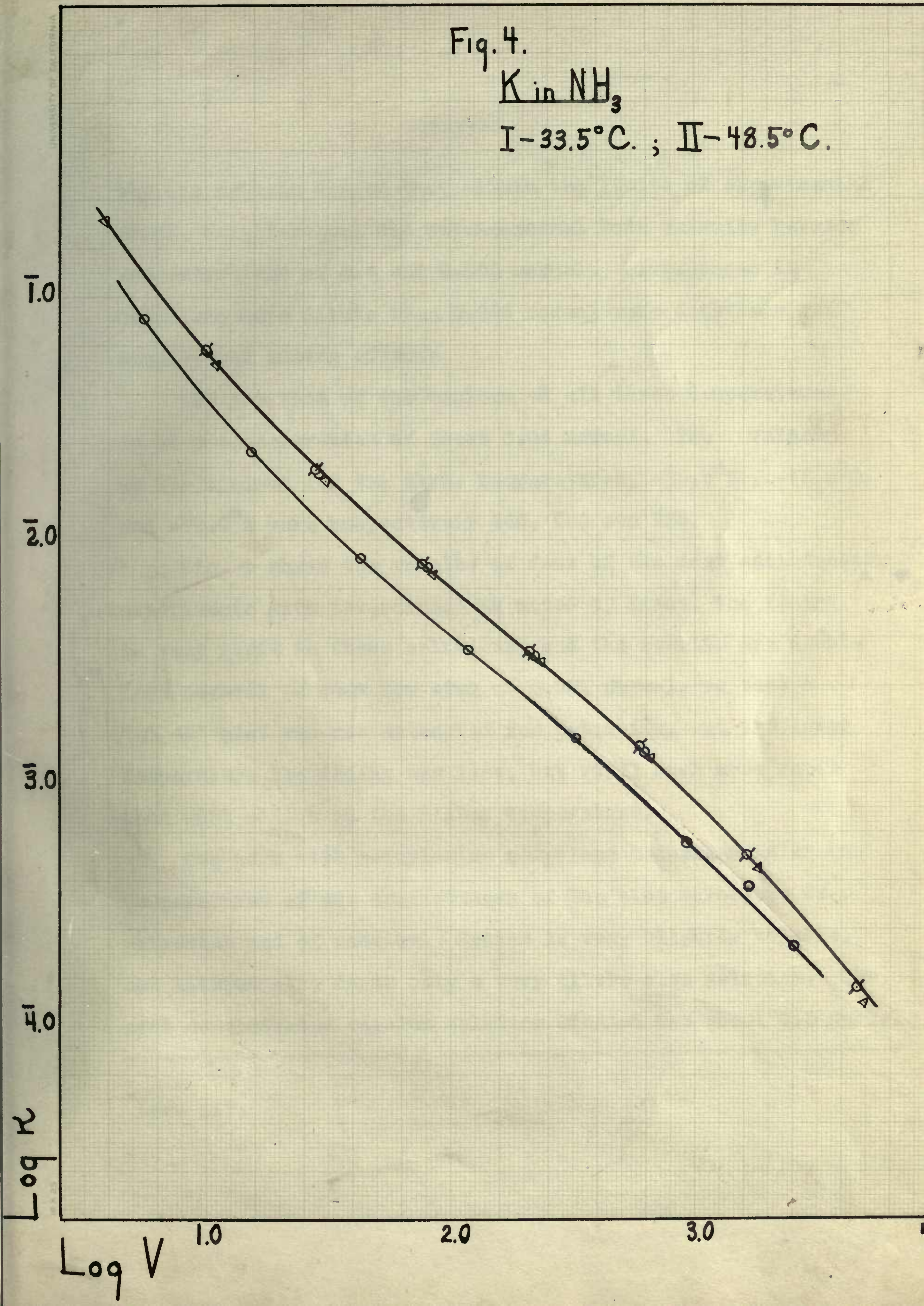

Fig. 4.
K in NH_3
I − 33.5°C. ; II − 48.5°C.
$\bar{1}.0$
$\bar{2}.0$
$\bar{3}.0$
$\bar{4}.0$
Log κ
1.0
2.0
3.0
Log V

the two methods showed that within the limits of experimental error, weight-normal and volume-normal data coincide between concentrations of 0.4 and 0.005 normal. Divergences in solutions more dilute than 0.005 normal were doubtless not density but fading effects.

The position of the minimum at all three temperatures is at a concentration of about 0.04 normal. The values at the minimum for the three temperatures, -33.5°C., -48.5°C. and -70.0°C were respectively 460, 360 and 235.

Fig. 4 shows the results of four of the most satisfactory experiments with potassium. As noted by Kraus[1], the fading is very rapid in these solutions, and the results are doubtless several percent low even at 0.001 normal, so that a "Λ_0-k" plot was not attempted for potassium. At the lower temperature the fading was less, but still much more rapid than with sodium at the higher temperature.

The work with methylamine comprised measurements at two temperatures of the conductances of the blue solutions of potassium and of caesium. Sodium is very slightly soluble, and lithium also forms only a very dilute blue solution. The most concentrated caesium solution studied was about 0.3 normal.

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[1] Loc. cit.

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The work with methylamine comprised measurements at two temperatures of the conductances of the blue solutions of potassium and of caesium. Sodium is very slightly soluble, and lithium also forms only a very dilute blue solution. The most concentrated caesium solution studied was about 0.3 norm

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[1] Loc. cit.

Table III

Conductance of Caesium and of Caesium Iodide in Methylamine.

-33.5° C.

Series I

No.	log k	log V	Λ
1	$\bar{3}.556$	1.145	50.3
2	$\bar{3}.160$	1.591	56.4
3	$\bar{4}.839$	2.035	74.9
4	$\bar{4}.529$	2.476	101.2

Series II

No.	log k	log V	Λ
1	$\bar{2}.302$	0.527	67.5
2	$\bar{3}.707$	0.985	49.9
3	$\bar{3}.273$	1.453	53.3
4	$\bar{4}.926$	1.911	68.8

Series III

No.	log k	log V	Λ
1	$\bar{3}.048$	1.728	59.7
2	$\bar{4}.740$	2.171	81.5
3	$\bar{4}.418$	2.620	109.2
4	$\bar{4}.087$	3.061	140.7
5	$\bar{5}.703$	3.503	159.6

-48.5° C.

Series IV

No.	log k	log V	Λ
1	$\bar{3}.850$	0.708	36.1
2	$\bar{3}.362$	1.163	33.5
3	$\bar{3}.005$	1.606	40.9
4	$\bar{4}.695$	2.049	55.5
5	$\bar{4}.386$	2.492	75.5

Series V

No.	log k	log V	Λ
1	$\bar{3}.691$	0.880	37.3
2	$\bar{3}.233$	1.325	36.2
3	$\bar{4}.897$	1.768	46.3
4	$\bar{4}.577$	2.212	61.6
5	$\bar{4}.257$	2.653	81.3

Series VI

No.	log k	log V	Λ
1	$\bar{4}.588$	2.233	66.3
2	$\bar{4}.302$	2.678	95.5
3	$\bar{5}.972$	3.125	125.1
4	$\bar{5}.612$	3.569	151.8
5	$\bar{5}.187$	4.011	157.8

Table III (concluded)

Series VII (Caesium Iodide)

-33.5°C				-48.5° C.			
No.	log k	log V	Λ	No.	log k	log V	Λ
1	$\bar{4}.797$	1.296	12.4	1	$\bar{4}.747$	1.288	10.8
2	$\bar{4}.370$	1.744	13.0	2	$\bar{4}.326$	1.736	11.5
3	$\bar{4}.022$	2.193	16.4	3	$\bar{5}.978$	2.185	14.6
4	$\bar{5}.708$	2.642	22.4	4	$\bar{5}.670$	2.634	20.1
5	$\bar{5}.430$	3.091	33.2	5	$\bar{5}.384$	3.083	29.3

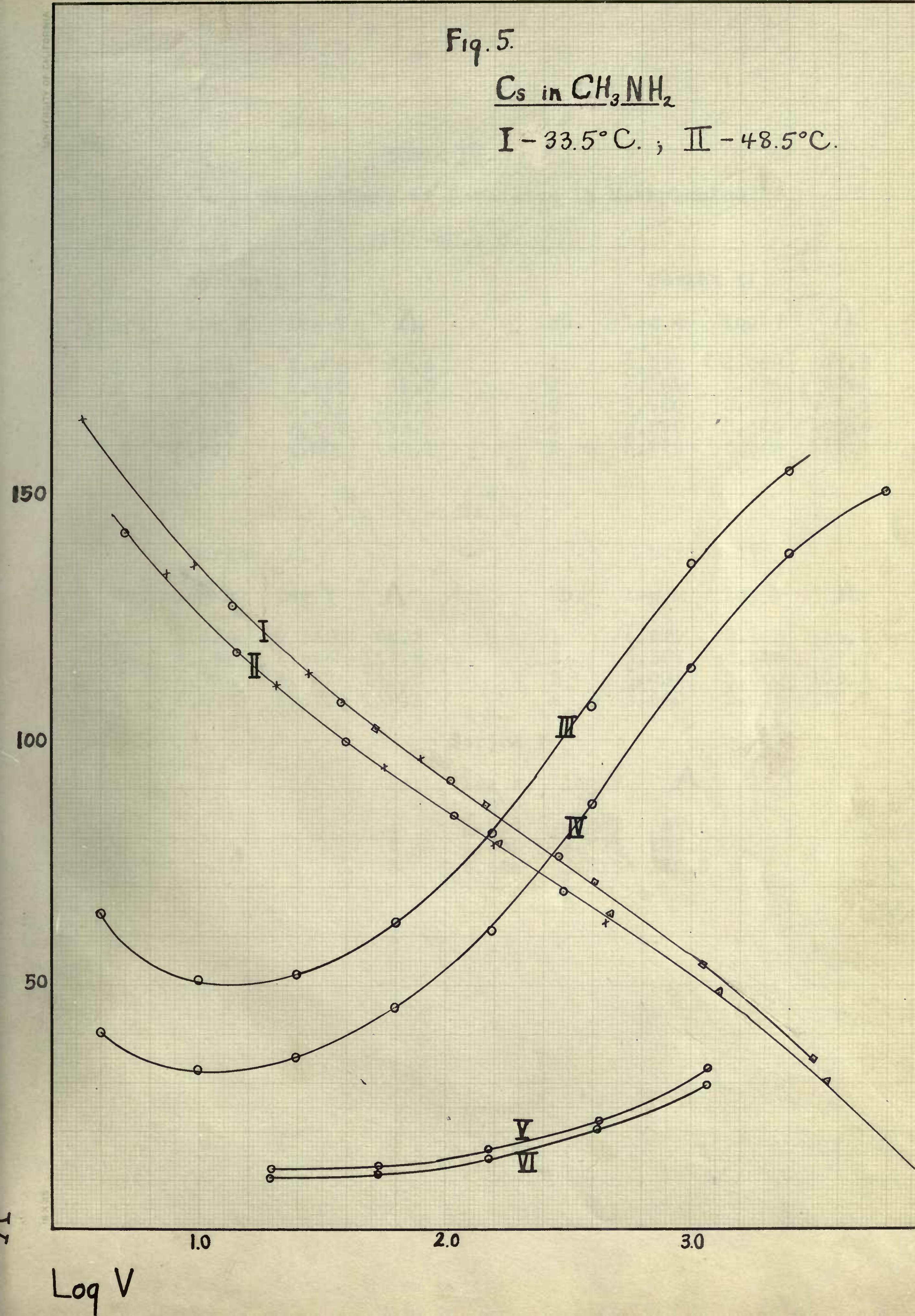


Fig. 5.
Cs in CH_3NH_2
I - 33.5°C. ; II - 48.5°C.
150
100
50
I
II
III
IV
V
VI
1.0
2.0
3.0
Log V

Table IV

Conductance of Potassium in Methylamine

-48.5° C.

Series I

No.	log k	log V	Λ
1	$\bar{4}.394$	2.408	63.4
2	$\bar{4}.049$	2.869	82.8
3	$\bar{5}.721$	3.314	108.4
4	$\bar{5}.366$	3.758	133.1
5	$\bar{6}.891$	4.201	152.1

Series II

No.	log k	log V	Λ
1	$\bar{4}.592$	2.088	47.9
2	$\bar{4}.269$	2.534	63.6
3	$\bar{5}.940$	2.977	82.6
4	$\bar{5}.590$	3.425	103.6
5	$\bar{5}.229$	3.868	125.1

-33.5° C.

Series III

No.	log k	log V	Λ
1	$\bar{4}.426$	2.542	92.9
2	$\bar{4}.096$	2.984	117.5
3	$\bar{5}.726$	3.427	142.3
4	$\bar{5}.303$	3.870	149.1

Series IV

No.	log k	log V	Λ
1	$\bar{4}.679$	2.143	66.4
2	$\bar{4}.357$	2.586	87.7
3	$\bar{4}.009$	3.030	109.4
4	$\bar{5}.640$	3.476	130.7

Series V

No.	log k	log V	Λ
1	$\bar{4}.514$	2.328	69.6
2	$\bar{4}.250$	2.773	105.5
3	$\bar{5}.884$	3.218	126.5

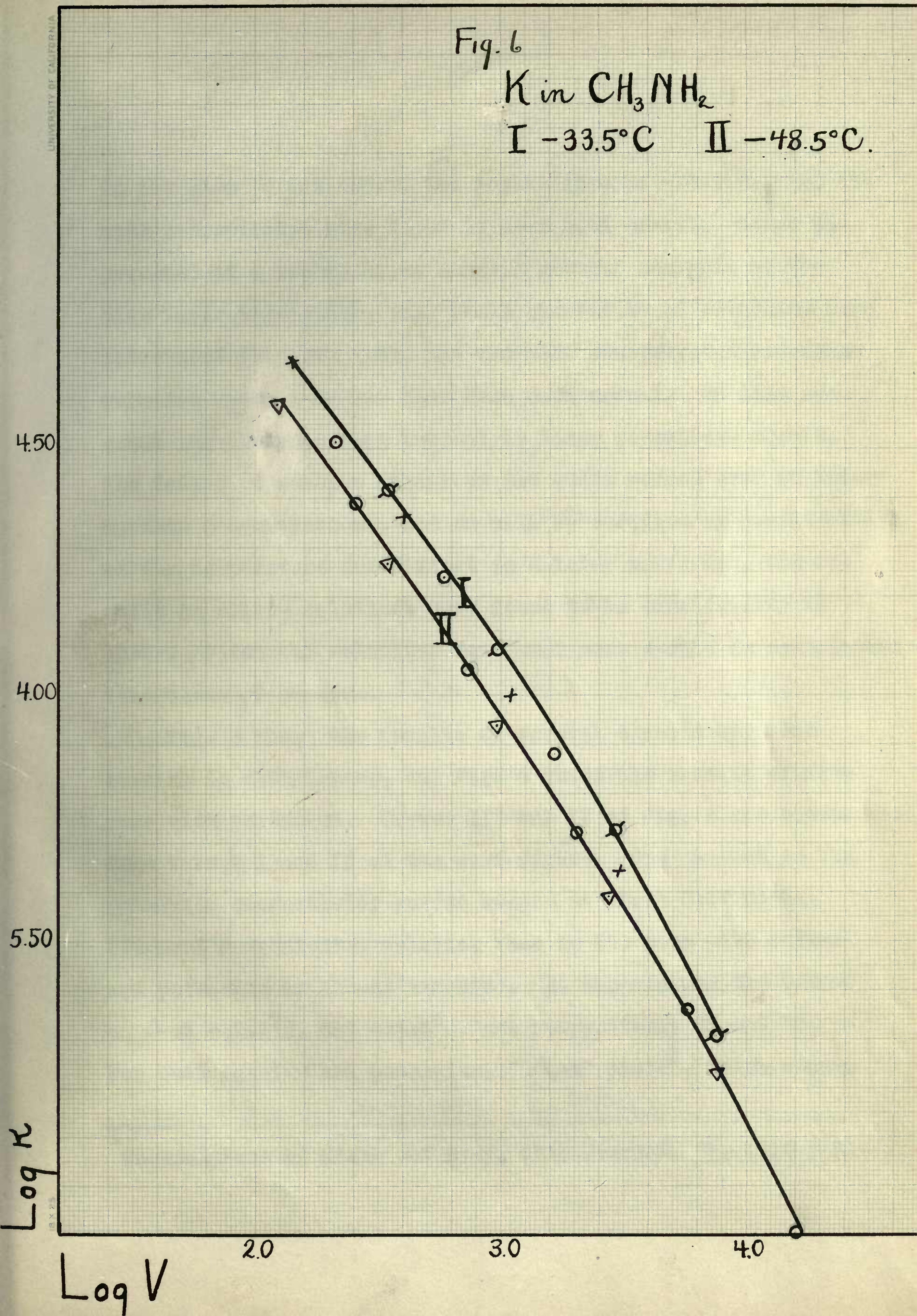
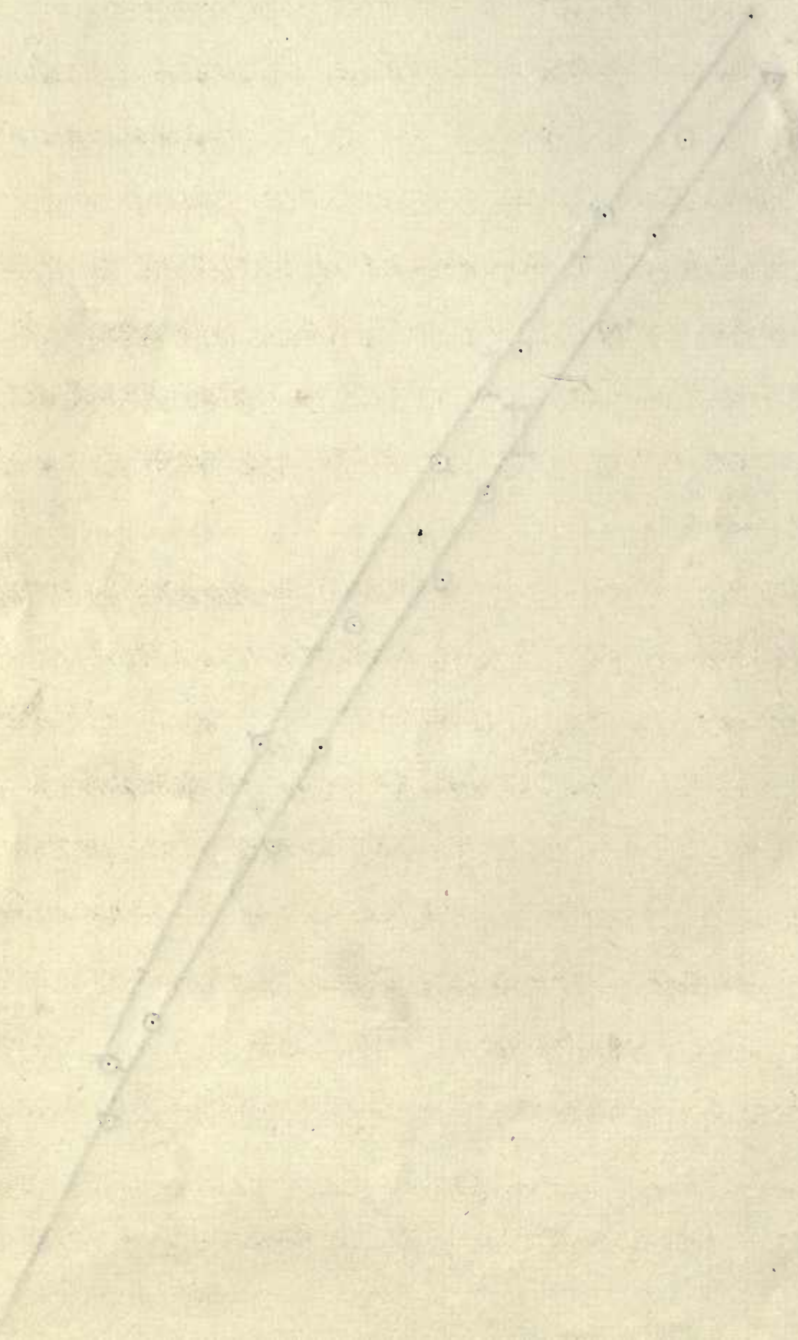


Fig. 6
K in CH_3NH_2
I −33.5°C II −48.5°C.



In the case of potassium, two layers form at -33.5°C., and the most concentrated blue layer is near 0.01 normal. Since the presence of a bronze layer makes a correct analysis of the blue layer impossible, only small quantities of potassium were introduced into the cell, and the most concentrated potassium solution determined was less than 0.01 normal. On this account the analyses were subject to large percentage errors. The fading of caesium solutions was quite marked even at intermediate concentrations, and as will be verified by consideration of the temperature coefficient in a later paragraph, the results in dilute solutions were found to be considerably in error. Potassium solutions were much more stable in methylamine than those of caesium.

Fig. 3 shows the results of several experiments with caesium in methylamine, and Fig. 4 shows the results of five runs with potassium. Curves III and IV of Fig. 3 are constructed from Curves I and II of the same figure. The minimum in the molecular conductivity curves occurs at about 0.07 normal (in more concentrated solution than is the case with sodium and potassium in liquid ammonia). At the minimum the values of Λ at -33.5°C. and -48.5°C. are respectively 51 and 33. For both caesium and potassium, "$\Lambda_{\circ}$-k" plots[1], which assume

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[1] Nomenclature of Kraus and Bray, This Journal, 35, 1315 (1913).

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[1] Nomenclature of Kraus and Bray, This Journal, 35, 1315 (191

the validity of the mass law, were constructed, and led to the following values:

Temp.	Metal		k(mass law const.)
-33.5	K	159	21.4×10^{-4}
-48.5	K	144	11.2×10^{-4}
-33.5	Cs	188	19.4×10^{-4}
-48.5	Cs	174	13.9×10^{-4}

A single run was also made with caesium iodide[1] in methylamine, and the results of this experiment appear in Fig. 3, Curves V and VI. The position of these curves is substantially the same as that for potassium iodide in methylamine given by Franklin and Gibbs[2]. "Λ_0-k" plots for caesium iodide led to the following values:

Temp.		k(mass law const.)
-33.5	60.6	4.91×10^{-4}
-48.5	56.2	4.64×10^{-4}

Discussion of Results.

The true temperature coefficient in dilute solutions is independent of temperature. In Table V of his recent article

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1 Caesium chloride was found to be insoluble.

2 Franklin and Gibbs, This Journal 29, 1391 (1907).

upon conductance in liquid ammonia[1], Kraus calculates values for $\Delta(1/R)/\Delta t(1/R_{33}) \times 100$, and this quantity increases rapidly with temperature. Evidence that the true temperature coefficient d(ln k)/dt is independent of temperature in dilute solutions is presented in Fig. 3. The three upper points are values for log R taken from Fig. 2 at 0.004 normal, and moved along the log R axis until the value at $-33.5^{\circ}C$ agrees with that of Kraus. The five lower points are Kraus's values for log R in "dilute solution" over a higher range of temperature. Weight is given to the points at the lower temperature where the fading was less. A straight line seems to be justified, since the aberration of the points at the higher temperatures is in the direction to be expected from fading.

At concentrations near the minimum there was evidence of a larger temperature coefficient at the higher temperature in the case of both sodium and potassium, but the effect was scarcely beyond the limit of experimental error, and could not be established with certainty.

In Table V is a summary of temperature coefficients calculated from the log k curves in the preceding figures. The values of d(log k) were taken directly from the plots. In the

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[1] Loc. cit.

Table V

Summary of Temperature Coefficients

Log V	Temp. Range	Solute	Solvent	d(ln k)/dt $\times 10^3$	Average
1.4	-33 to -48	Na	NH_3	20.9	
2.4	"	"	"	20.7	20.4
1.4	-48 to -70	"	"	18.6	
2.4	"	"	"	21.6	
1.4	-33 to -48	K	NH_3	27.4	29.1
2.4	"	"	"	30.7	
2.0	-33 to -48	K	CH_3NH_2	20.6	19.8
3.0	"	"	"	19.0	
1.0	-33 to -48	Cs	CH_3NH_2	27.6	23.9
2.0	"	"	"	20.3	
3.0	"	"	"	9.2 (fading)	
1.3 -3.0	"	CsI	CH_3NH_2	7.7	7.7

last column of Table V appear the values of d(ln k)/dt at one or more dilutions for each solute, and also an average value for each solute.

The temperature coefficients are about the same in the two solvents. The rapid decline in the temperature coefficient of caesium in methylamine is ascribed to fading. For a 0.001 normal potassium solution, in which the fading was much slower, the temperature coefficient is still 19×10^{-3}, whereas at the same dilution in a caesium solution the value has fallen to 9×10^{-3}.

It has been pointed out by Kohlrausch[1] that the temperature coefficients of conductivity and viscosity in aqueous solutions of most salts are approximately the same. Hydrogen and hydroxyl ions are exceptions to this rule, the temperature coefficients of conductivity being abnormally low. Johnston[2] studied the relationship between viscosity and conductivity over a wide range of temperature in water and in non-aqueous solvents, and showed that the equation,

$$\Lambda = k\phi^{m},$$

where ϕ is the fluidity, and m and k are constants, appears to be generally applicable. The value of m is usually very nearly unity. Hydrogen and hydroxyl ions are again exceptional.

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1 Kohlrausch und Holborn, Das Leitvermogen der Elektrolyte, p.127. (Teubner, Leipzig und Berlin, 1916)

2 This Journal, 31, 1010(1909).

We may remark in passing that the low value of the temperature coefficient of conductivity of these ions might be accounted for if we assume the conductivity to be due in part to the liberation of a hydrogen or a hydroxyl ion at one end of a chain of water molecules, and a simultaneous binding of a hydrogen or a hydroxyl ion at the other end of the chain, without actual migration of the ions through the solution, as has been suggested by various authors[1] to account for the abnormally high conductance of these solutions. For, if we assume such chains of water molecules to become less stable at the higher temperatures, the diminution in this type of conduction would counteract the increase due to the diminishing viscosity of the solution, and thus give an abnormally low temperature coefficient. If we assume the rule of Kohlrausch to hold for methylamine, the temperature coefficient of the conductivity of all salts in this solvent should be approximately equal to that of caesium iodide. If this is true, the temperature coefficient of conductivity of the alkali metals in methylamine is abnormally high. This could be accounted for by a decreased solvation of the electrons with rise in temperature,- as was assumed by Gibson and Argo[2] as a possible explanation of the

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1 Lewis, This Journal, 34, 1642 (1912); Latimer and Rodebush, Ibid., 42, 1432 (1920).

2 Loc. cit.

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[1] Lewis, This Journal, 34, 1642 (1912); Latimer and Rodebush, Ibid., 42, 1432 (1920).

[2] Loc. cit.

diminution in the coefficient of absorption of these solutions with increasing temperature.

In order to account for the deviation from Beer's Law for the shorter wave-lengths in solutions of the alkali metals in methylamine, Gibson and Argo assumed the absorption at these wave-lengths to be partly due to unionized metal. Since the solutions in ammonia do not show this deviation from Beer's Law, they assumed the ionization in ammonia to be more complete than in methylamine. The dissociation constant for the metals in ammonia is greater than that in methylamine, but the difference is hardly sufficient to account for the deviations which they observed. The deviation from Beer's Law may nevertheless be due to unionized metal, for the absorption due to unionized meta in ammonia may not be in the visible spectrum. This point could not be decided without a knowledge of the absorption curve in ammonia at other wave-lengths.

We have already mentioned that the conductivity curves of the metals in ammonia and in methylamine are of the same general type, the conductivity diminishing at first according to the mass law in dilute solutions, becoming greater than would be predicted from the mass law in more concentrated solutions, until a minimum in the conductivity is reached, after which the conductivity rises very rapidly as the concentration is further increased. The minimum is approximately the same for

all the metals in any one solvent, but occurs at a somewhat lower concentration in ammonia than in methylamine. If we assume the increase in conductivity to the higher concentrations to be due to the influence of free ions in the solution, which cause a diminution in the electrical forces,- for much the same reason that an increase in the dielectric constant would cause a diminution in these forces,- we should expect a deviation from the mass law to occur at lower concentrations in a solution which is highly ionized than in one which is less so. We have seen that the metals are more highly ionized in ammonia than in methylamine; hence the solutions in ammonia, other things being equal, should show a minimum at lower concentrations than those in methylamine, as is actually observed. The extreme rapidity of the increase in conductivity at concentrations beyond the minimum points to a rapid diminution in the solvation of the electrons as the concentration is increased. This would seem to,indicate that the force binding the electron to the solvent is electrical in character, and is diminished in concentrated solutions for the same reason that the ionization of the metal is increased, - namely owing to a diminution in the electrical forces due to the presence of free ions in the solution.

A certain amount of support for the assumption that the

attraction between the electron and the solvent is electrical in character is given by the fact that the absorption maximum in methylamine occurs at a shorter wave-length than in ammonia. In the latter solvent the measurements of Gibson and Argo[1] appear to indicate an absorption maximum in the infra-red. The dielectric constant of ammonia is greater than that of methylamine and we should therefore expect the electron to be less firmly bound in ammonia than in methylamine if the binding force is electrical in character. Determinations of the absorption maxima of lithium in ethylamine and propylamine, and a determination of the dielectric constants of these solvents should throw light on this question.

NO